

Strong electron correlations in cobalt valence tautomers

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We have examined cobalt based valence tautomer molecules such as $\text{Co}(\text{SQ})_2(\text{phen})$ using density functional theory (DFT) and variational configuration interaction (VCI) approaches based upon a model Hamiltonian. Our DFT results extend earlier work by finding a reduced total energy gap (order 0.6 eV) between high temperature and low temperature states when we fully relax the coordinates (relative to experimental ones). Furthermore we demonstrate that charge transfer picture based upon formal valence arguments succeeds qualitatively while failing quantitatively due to strong covalency between the Co $3d$ orbitals and ligand p orbitals. With the VCI approach, we argue that the high temperature, high spin phase is strongly mixed valent, with about 30% admixture of Co(III) into the predominantly Co(II) ground state. We confirm this mixed valence through a fit to the XANES spectra. Moreover, the strong electron correlations of the mixed valent phase provide an energy lowering of about 0.2-0.3 eV of the high temperature phase relative to the low temperature one. Finally, we use the domain model to account for the extraordinarily large entropy and enthalpy values associated with the transition.

I. INTRODUCTION

Transition metal complexes with redox active ligands have been the subject of extensive studies in recent years. Of particular interest are the valence tautomers based upon semiquinone and catecholate groups ligated to transition metal ions [1,2]. These molecules have intrinsic interest as candidates for mechanical and magnetic switching devices activated by temperature, pressure, or irradiation. They also present coordination environments and structural and magnetic conformation reminiscent, at least, of the local properties in certain allosteric metalloproteins [3].

In this paper, we focus on the cobalt based valence tautomers of generic (high temperature) form $\text{Co}(\text{SQ})_2\text{L}_p$, where SQ represents a semiquinone ligand complex with formal charge -1 and spin 1/2, and L_p represents a neutral redox passive counterligand such as phen, py_2X ($\text{X}=\text{O}, \text{Se}, \text{S}, \text{Te}$), tetramethylmethylenediamine (tmmda), or tetramethylethylenediamine (tmeda). When cooled in frozen organic solvents such as toluene, or in molecular solid form (typically under pressure), these molecules undergo a transition, in a narrow temperature regime (typically between 100 and 400K), from a high spin, high volume form, to a low spin, low volume form [4–9]. The moment changes from order $4\text{--}6 \mu_B$ at high T to $2 \mu_B$ at low T , while the bond lengths of the inner coordination sphere typically decrease by about 10%, about 0.2\AA .

Traditionally, it is assumed that there is a charge transfer from Co to the SQ ligands concomitant with the transition, with the enhanced ligand field splitting arising from the bond contraction favoring low spin Co(III). This picture accounts for the observed susceptibility data, and is consistent with observed hyperfine splittings, optical absorption.

However, there remain some puzzles in this accepted description of the valence tautomers, notably:

- (1) On the theoretical side, density functional calculations [11] have so far provided modest support to the above description, yielding stable high spin states for the high temperature geometry, and stable low spin states for the low temperature geometry. However, more Co electron charge is found at low T .
- (2) For the $\text{Co}(\text{SQ})_2(\text{phen})$ complex, x-ray absorption near edge spectra (XANES) spectra measured for the Co K-edge [10], there is additional spectral weight at high energies (about 2-3 eV above the XANES peaks associated with transitions to $3d$ states) which has not yet been accounted for.
- (3) The estimated entropy change ΔS at the transition inferred from fits to the effective moment is extraordinarily large, of order $10\text{--}15 R$ [5], which is difficult to account for from softened vibrational modes at higher T . Concomitantly, a large enthalpy of order 0.3 eV/molecule is required. Direct measurements of ΔS [12] for molecular solid forms give, on the other hand, a value of about $1.2 R$, consistent with the spin entropy change, which gives $\Delta H \approx 0.03 \text{ eV/molecule}$.

Motivated by these experimental and theoretical puzzles, we have set about to extend the description of the cobalt valence tautomers driven in large measure by a desire to assess the role of strong electron correlations in such systems. To this end, we have: (i) performed new, spin polarized, fully relaxed density functional theory calculations. These calculations provide an energy lowering of the high T -low T splitting which partly reduces the disagreement between earlier DFT calculations and experiment. A Mulliken population analysis reveals 0.2 fewer Co $3d$ electrons for the high- T form when compared to the low- T form, in marked contrast to the stan-

dard picture. We demonstrate, through an examination of the projected densities of states, that the arguments based upon formal oxidation states are qualitatively correct when one identifies the overall molecular orbitals derived from the nominal e_g symmetry about the Co site. (ii) We have developed a model Hamiltonian for the active electronic states which we solve by a variational wave function calculation which includes strong electron correlation effects on the Co site (outside DFT). This calculation amounts to configuration interaction with a physically motivated basis set reduction which has proven useful for analyzing solid state systems. We find a significant further reduction in the high- T /low- T energy difference, with stronger electron correlation effects in the high- T phase (which has 0.3 less Co 3d electrons than the low- T phase). In particular, at high- T the high spin Co(II) significantly admixes with a high spin Co(III) state in which an SQ electron antiferromagnetically screens the Co moment. We show that this a good quantitative account for the K-edge XANES data discussed above. (iii) We show that a domain model [13,14] can resolve the discrepancy between inferred and direct measurements of $\Delta S, \Delta H$. Specifically, we show that existing experimental data is inconsistent with the assumption of a random mixture of high- T and low- T forms of the tautomer and is best explained by assuming the molecules form clusters of size ~ 30 -50.

We stress that this description of the high- T phase of the valence tautomers makes them *mixed valent* in the sense used in the physics community to describe lanthanide compounds such as CeSn_3 or SmS , in which the ground state is a quantum superposition of states with predominantly two to three well defined valences for the rare earth ion. This mixed valence is distinct from the multi-site mixed valence of, e.g., the Creutz-Taube molecule. We distinguish this single site mixed valence from *covalence*, which is applicable to strong molecular orbital admixture at the single particle level. In this sense, a mixed valent single ion is intermediate between fully localized and fully covalent. Such molecular states have already been noted, e.g., in the case of cerocene [15], where formal valence arguments generate the expectation of diamagnetic, tetravalent Ce ions, while observations yield temperature independent paramagnetism. The Ce ion is mixed valent in this case.

We discuss the DFT results in Sec. II, the many body theory in Sec. III, the domain model in Sec. IV, and conclusions in Sec. V.

II. ELECTRONIC STRUCTURE CALCULATIONS

A. Computational Method

We carry out the spin-polarized electronic structure calculations using the *ab initio* code SIESTA [16,17].

The Kohn-Sham equations are solved with the exchange-correlation calculated using the generalized-gradient-corrections(GGA) approximation, in the fully *ab initio* version of Perdew, Burke and Ernzerhof [18]. We use Troullier-Martins norm-conserving pseudopotentials [19] in the Kleinman-Bylander form [20]. For Co, we use non-linear partial-core corrections to account for exchange and correlation effects in the core region [21]. The basis set orbitals are obtained using the method of Sankey and Niklewski [22], generalized for multiple- ζ and polarization functions [23]. For the Co atom the basis set consisted of double- ζ 3d and 4s orbitals with 4p polarization orbitals. For C,N and O the basis set was double- ζ 2s and 2p orbitals whereas for H it was double- ζ 1s orbitals.

The initial atomic coordinates are obtained using the experimentally determined high-temperature and low-temperature geometries for the phen complex. In both cases, following previous work [11], the tertiary *butyl* groups were removed and replaced with H atoms (at a distance $\sim 1\text{\AA}$ from the C atoms). The supercell approximation was used and a cubic supercell of dimension 38 Bohr was taken to ensure sufficient vacuum between neighboring tautomer molecules. The results obtained were checked for convergence by increasing supercell size to 45 Bohr. Conjugate-gradient relaxation was performed on the system, with the experimental geometries providing the set of initial coordinates, to determine the minimum energy configuration within DFT. The atoms were allowed to relax till the force on each atom was less than 0.04 eV/\AA . The electronic structure was determined both for the initial geometry and the final relaxed geometry and the results are presented in the following.

B. Results

The ground-state energetics obtained by us for the experimental geometries are in agreement with previous *ab initio* calculations [11]. For the high-temperature geometry, the electronic structure calculation yields high-spin ($\sim 3/2$) Co coupled ferromagnetically to spin $1/2$ on each of the ligands. Furthermore we find that the low-spin configuration cannot be stabilized for the high-temperature geometry. In contrast, for the low-temperature geometry, the low-spin (~ 0) configuration is stabilized and the high-spin configuration is unstable. In the low temperature geometry there is a net spin $1/2$ for the complex which is located on the oxygen ligands. Furthermore, we find a net spin of 0.06 on the Co ion, consistent with the observed hyperfine splitting of 30G or less [5], reduced by an order of magnitude compared to, e.g., metallic Co. Thus, our results are in agreement with experimental data which show a transition from a high-spin state to a low-spin state as the temperature is decreased.

The reason is of course, not complicated: the increased $3d$ - $2p$ hybridization upon contraction increases the hybridization induced ligand field splitting on the Co site, which disfavors Hund's rule alignment of the spins (the point charge contribution increases as well). The entropy cost is offset by the energy gain from increased ligand field energy.

The ground-state energy difference between the two states *without relaxation from the experimental geometry* is found to be 1.3 eV, which is in good agreement with the previously obtained value of 1.2 eV. However this energy difference is too high to be consistent with the room-temperature transition observed in the system. Experimentally the enthalpy change (ΔH) between the two states is inferred from fits to the magnetic moment to be ~ 0.3 eV/molecule [5] which is much lower than the theoretical value (as mentioned, the lone direct specific heat measurement suggests $\Delta H \approx 0.03$ eV/molecule). However, even this experimentally inferred value for the enthalpy corresponds to an entropy change of $\sim 14 R$ which is unphysically large. Thus we are faced with a discrepancy between the experimental results and the energetics obtained using DFT.

This discrepancy can be partially resolved by noting that the experimentally determined ground-state geometry can differ slightly from the DFT ground-state geometry. Thus to allow the system to relax to the DFT ground-state configuration, we performed conjugate-gradient relaxation starting from the experimental geometries. Relaxing the geometries resulted in a substantial lowering of the energy difference between the high-spin and low-spin configurations to 0.6 eV, as compared to 1.3 eV for the unrelaxed geometries. In this relaxation process, the bond distances between Co and ligands changes very little, and thus the relaxed geometry might be argued as a better comparison point for experiment. In a previous study for the unrelaxed experimental geometries, Adams *et al* [5] obtained a lowering of the ground-state for the high-spin configuration by performing a 'broken-symmetry' run. However, we have found that the broken-symmetry configuration is not stable and upon relaxation the ground-state configuration is given by the ferromagnetic alignment of the ligand spins to the Co spin. However, the ground-state energy difference obtained after relaxation is still too high to be consistent with the low transition temperature and it indicates that correlation effects which are not included in DFT play a significant role in determining the ground-state energies.

Performing the Mulliken population analysis for the relaxed geometries leads to another discrepancy with the traditional interpretation of valence tautomerism. In this framework, the transition is described as a spin crossover phenomenon associated with charge transfer from the metal to the ligands. However the DFT results indicate that the net d -charge *increases* in going from the

high-spin geometry (7.1) to the low-spin geometry (7.3). This should be contrasted with the traditional picture in which we should expect the net d -charge to be lower by 1 in the low-spin geometry due to charge transfer to the ligands.

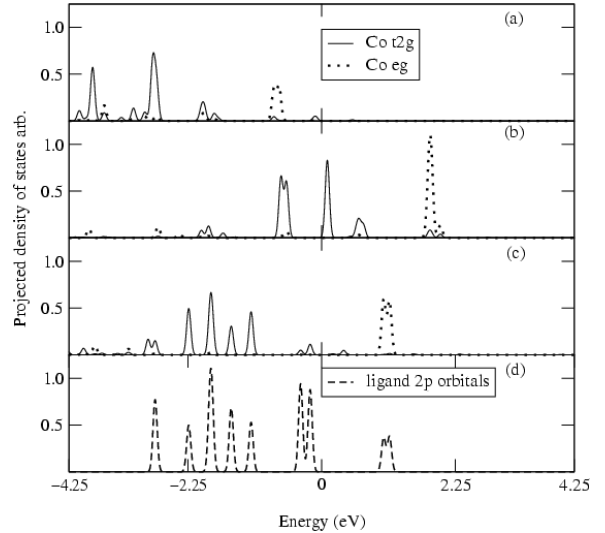


FIG. 1. Partial densities of states (PDOS) for Co-valence tautomers in the vicinity of the first ionization level. (a) Co 3d-projected PDOS for the majority spin in the high temperature phase. (b) Co 3d-projected PDOS for the minority spin in the high temperature phase. (c) Co 3d-projected PDOS for majority spin in the high temperature phase. There is negligible difference in this case between majority and minority spins. (d) PDOS jointly projected to SQ/CAT 2p and Co 3d levels in the low temperature phase. Note that the formal e_g levels, for example, are strongly covalently admixed between the ligands and the Co ion.

A resolution of this discrepancy is reached by analyzing the transition in terms of molecular orbital theory and studying the projected density of states (PDOS) for the two geometries. In terms of molecular orbital theory, the transition can be summarized as follows. The d orbitals on the metal are split into the t_{2g} and e_g groups. The metal e_g levels mix with the ligand σ orbitals to form molecular orbitals which are bonding and antibonding in character. The bonding levels are expected to be ligand dominated and the antibonding levels metal dominated. The t_{2g} levels don't mix with the σ orbitals (ignoring, for simplicity, the mixing with the ligand π orbitals) and the splitting between the t_{2g} levels and the antibonding molecular orbitals (dominated by metal e_g levels) is what corresponds to the crystal-field splitting. In the high temperature geometry the lower crystal-field splitting stabilizes the high-spin phase in which the antibonding e_g orbitals are occupied by two electrons and the t_{2g} levels have 1 hole. In the low temperature geometry the e_g levels are unoccupied and the t_{2g} levels are filled and the

remaining electron is transferred to the ligands. Thus we have a crossover from a high-spin configuration to a low-spin configuration associated with charge transfer from the metal to the ligands.

A detailed analysis of the PDOS, shown in Fig. 1, for both the high-spin and low-spin geometries reveals that the above picture is indeed accurate, and yet it is also consistent with the DFT result that the net d -charge is greater in the low T phase. This is explained as follows: In the high T phase there is an occupancy of the $e_g - \sigma$ antibonding molecular orbitals of 2 electrons in the spin-up channel. In the low T phase one of these electrons gets transferred to the Co t_{2g} level and the other is transferred to the ligand SQ level. However this does not translate into a lowering of charge on the Co atom by one. There is significant covalency between the metal- e_g levels and the ligand- σ orbitals. So when 2 spin-up electrons are transferred from the $e_g - \sigma$ antibonding orbitals that corresponds to a loss of just 1.4 for the Co atom and not 2. On the other hand because there is greater overlap in the low-T phase there is greater metal contribution to the occupied $e_g - \sigma$ bonding orbitals (which are ligand dominated). The difference between the metal contributions to the $e_g - \sigma$ bonding orbital is ~ 0.6 (higher in the low T phase). So the net metal e_g occupancy in going from high T to low T changes by $-1.4 + 0.6 = -0.8$ i.e by less than 1 electron and not 2 as the formal picture indicates. This is more than compensated by the increase in the occupancy of the t_{2g} level by 1 and hence we see that the net charge *increases* in the low T phase.

Thus we have seen that the DFT results support the traditional qualitative picture for valence tautomerism at the same time clarifying that there is no effective charge transfer in the system. However there is still a significant discrepancy between the calculated and observed energy differences between the two states. In the next section we will explore the role of correlation effects in reducing this discrepancy.

III. VARIATIONAL MANY BODY THEORY

In this section, we show that electron-electron interaction effects can provide a further reduction of ΔH beyond DFT, and that they provide an explanation for heretofore unexplained spectral intensity in the high-T XANES spectra. Moreover, they confirm that like cerocene, the high-T phase of the valence tautomers is mixed valent in the sense used within the physics community to describe SmS, CeSn₃ and other intermetallic compounds.

A. Model Hamiltonian

In order to investigate the possible role for correlation effects in the cobalt valence tautomers, we wish to

consider the simplest model that possesses the salient features that are commonly accepted as essential for the combined metal-ligand charge transfer (CT)/spin crossover of the tautomeric interconversion. We model this with an Anderson Impurity Hamiltonian [25], in which local electron correlation effects are treated accurately on the Co site, but neglected on the ‘metallic’ carbon rings.

We have taken the structure of the Co(phen) complex as the physical basis for our model. We represent the o-quinone ligands by their benzene ring skeletons and the oxygen atoms which are nearest neighbor to the metal site, and neglect octahedral symmetry breaking at the Co site. The model system therefore consists of the cobalt atom, the $3d$ -levels split by the cubic field arising from the local six-fold coordination of the oxygen atoms, the nitrogen atoms of the (N-N) complex, and the aromatic rings of the semiquinones.

We restrict our model to the electronically active π orbitals of the semiquinone ligands and the $3d$ t_{2g} and e_g orbitals of the Co ion.

The LCAO Hamiltonian using second-quantized notation for the simple model we have just described is

$$\mathcal{H}_0 = - \sum_{i\alpha, j\beta, \sigma} t_{i\alpha j\beta} c_{i\alpha\sigma}^\dagger c_{j\beta\sigma} \quad (1)$$

where $c_{i\alpha\sigma}^\dagger$ and $c_{j\beta\sigma}$ are, respectively the fermion creation and annihilation operators of the aforementioned orbital set where i and j are site indices, α and β are orbital symmetry-adapted labels, and σ refers to the spin degeneracy. The $t_{i\alpha j\beta}$ are on-site energies for $i\alpha = j\beta$ and are electron-hopping integrals for $i\alpha \neq j\beta$. The on-site $3d$ energies are

$$\epsilon_{d\gamma\sigma} = \epsilon_{d\sigma} + \Delta\epsilon_{LF} \quad (2)$$

where

$$\Delta\epsilon_{LF} = - \sum_{i\alpha\sigma} \frac{|\langle i\alpha\sigma | \Delta V | d\gamma\sigma \rangle|^2}{\epsilon_{d\sigma} - \epsilon_p(i\alpha\sigma)} \quad (3)$$

$$+ \begin{cases} -0.4\Delta_0 & \text{if } \gamma = x^2 - y^2, 3z^2 - r^2 \\ 0.6\Delta_0 & \text{if } \gamma = xy, yz, xz \end{cases}$$

where ΔV is the potential barrier that an electron hopping from the Co atom to one of the ligand N or O atoms must tunnel through, i is the site sum over the 4 oxygens and 2 nitrogen and α refers to the three $2p$ -orbitals on those sites. γ sums over the degeneracy of irreps of O_h and $\epsilon_{d\sigma}$ is the bare d -electron energy while $\epsilon_p(i\alpha\sigma)$ are the ligand atom on-site energies. Δ_0 is the electrostatic contribution to the ligand field (LF). $\epsilon_{d\gamma\sigma}$ then plays the role of the on-site $3d$ -orbital energy in the model.

We include electron-electron interactions only for the Co $3d$ electrons. These are certainly the most significant owing to the more localized character of the states, and

experience with transition metal oxide solids show this to be a good starting assumption. Including also the spin-orbit coupling, we thus add to \mathcal{H}_0

$$\begin{aligned} \mathcal{H}_d = & U_d \sum_{\gamma\sigma \neq \gamma'\sigma'} n_{\gamma\sigma} n_{\gamma'\sigma'} + J_H \sum_{\substack{\gamma > \gamma' \\ \sigma > \sigma'}} \vec{s}_{\gamma\sigma} \cdot \vec{s}_{\gamma'\sigma'} \\ & + \sum_{i=1}^{N_d} \xi(\vec{r}_i) \vec{l}_i \cdot \vec{s}_i \end{aligned} \quad (4)$$

where U_d is the direct Coulomb integral and $J_H < 0$ is the ferromagnetic Hunds' rule exchange coupling. The occupancy operator is defined as $n_{\gamma\sigma} = d_{\gamma\sigma}^\dagger d_{\gamma\sigma}$ where $d_{\gamma\sigma}^\dagger$ creates an electron in the $3d$ -orbital γ with spin σ . \vec{l}_i is the orbital angular momentum of the i th d -electron and \vec{s}_i is the one-electron spin. $\xi(\vec{r}_i)$ is the free-ion parameter.

For parameters, we make use of the tabulated on-site energies and also the distance parameterizations of the hopping integrals of Harrison [26]. The hopping matrix elements are written as linear combinations of these integrals using Slater-Koster theory [27]. U_d and J_H are treated as model parameters. We are currently working to constrain these parameters from information gained through ab-initio methods. However, we may obtain reasonable estimates by fitting the results of the model calculation to X-ray absorption data. This places constraints on the charge transfer gap and also $U_{dc}-U_d$, which is the difference between the Coulomb integrals describing the core hole- $3d$ electron and $3d$ - $3d$ interactions, respectively.

The high and low temperature expressions of the charge transfer gap are given by

$$\begin{aligned} \Delta_{CT}^{\text{ht}} &\simeq \epsilon_d - 0.4\Delta_0 - \frac{3}{2}J_H + 6U_d - \epsilon_L \\ \text{and} \\ \Delta_{CT}^{\text{lt}} &\simeq \epsilon_d + 0.6\Delta_0 + 6U_d - \epsilon_L + 1.74\text{eV} \end{aligned} \quad (5)$$

where ϵ_L refers to the energy of an electron localized in a ligand orbital and 1.74 eV refers to the hybridization contribution to the ligand field splitting in the low-temperature geometry.

Thus, the Hamiltonian is essentially that of a single-impurity Anderson Model, with the Co ion providing the localized states and the SQ ligands playing the role of the 'metal'. Such a heuristic mapping to this model allows us to pursue a method of solution that we discuss in some detail in the next subsection.

B. Variational Wave Function

We proceed to solve for the ground state by performing a variational configuration interaction (VCI) within a restricted basis set consisting of the lowest energy single-Slater determinants. This amounts to diagonalizing the

Hamiltonian of Eqns.(1) and (4) within this basis of multi-electron wavefunctions. These determinants are built from the valence orbital set of our model.

For the 'impurity' model described above, the variational wavefunction method (VCI) has been shown to successfully describe transition metal or rare earth ions embedded both in metals and in metal oxides [28,29]. In the present molecular context we regard it as a physically motivated basis set reduction: we have 'divided' to conquer by emphasizing first the strongest source of electron-electron correlations, expanding in the hybridization about the atomic limit for the Co ion. This said, the approach yields results which are *non-perturbative* in V , and systematically controlled by two handles: (i) the spin+orbital degeneracy (the lowest order results within a restricted Hilbert space become exact for large degeneracy), with particle-hole excitations suppressed by inverse powers of the degeneracy relative to the starting state, and (ii) the presence of excitation gaps which suppress contributions from particle-hole excitations about the leading order configurations.

The composition of the valence electron ground state will indicate the significance of correlations. The repulsive nature of the Coulomb interaction will tend to drive d -electrons off the metal site. This should manifest as coherent quantum mechanical tunneling between states of n_d electrons and states belonging to the n_d-1 configuration (valence fluctuations). If such effects are insignificant, we should expect the type of single-determinant ground state that is treated very well within Hartree-Fock theory.

The construction of the many-body basis is briefly outlined. The states are Slater determinants that will consist of tensor products of cobalt states and ligand states, i.e. $|\Gamma\beta SM_S; L_\alpha\rangle$ where Γ is the crystal point-group irrep, β is its degeneracy, S is the total spin, M_S is the spin degeneracy. L_α is the ligand state label which is used only if the α^{th} orbital is occupied. Fig. 2 depicts the states we consider in the variational ansatz. We restrict our Hilbert space to the two low lying states containing 6 or 7 Co $3d$ electrons; strong Coulomb repulsion legislates against other configurations.

Magnetic susceptibility and x-ray absorption data, as well as first-principles calculations, have suggested the relevance of three closely-lying multiplets for the $3d$ -electrons: the 4T_1 of the high-spin (h.s.) $3d^7$ ($S = \frac{3}{2}$), the 2E of low-spin (l.s.) $3d^7$ ($S = \frac{1}{2}$), and the 1A_1 of l.s.- $3d^6$ ($S = 0$). In the spin sector, we consider only the stretched state of maximal M_S within the S manifold. These would be expected to be the lowest-lying due to the Hund's rule energy.

We also include an intermediate spin sector of states ($S = 1$, $3d^6(^3T_1)$ and 3T_2) which couple to the h.s. and l.s. states through the spin-orbit interaction and to l.s.- $3d^7$ by CT.

We assume that the SQ/CAT eigenstates of H_p are

adequately treated within the framework of Hückel theory. This provides the standard approximate method of dealing with π^* electrons. We employ these methods to find the unoccupied states of the two o-quinone ligands and also their decomposition onto the constituent atomic orbital basis. Once these states have been obtained, Eqns.(1) and (4) may be diagonalized within the truncated basis of tensor product states.

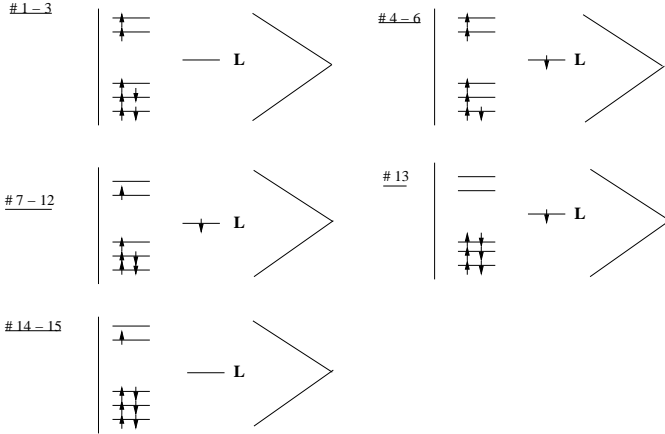


FIG. 2. Single-Slater determinants which comprise the many-body basis. States (1-3) are 4T_1 of h.s.- $3d^7$, (4-6) belong to 5T_2 of h.s.- $3d^6$, (7-12) are 3T_1 , 3T_2 of ($S=1$) $3d^6$, (13) is 1A_1 which is l.s.- $3d^6$, and (14-15) is 2E of l.s.- $3d^7$. L represents the doubly-degenerate spin-down LUMO of the quinone ligands.

C. Results

The Hamiltonian is diagonalized in both the high-T and low-T geometries using the optimized coordinates from the fully relaxed DFT runs. Fig. 3 is a histogram depicting how the quantum weight is distributed among the determinants of our variational ansatz ground state in both the high and low temperature phases. The high-T phase suggests a definite non-trivial role for correlations with a mixed valent state of 69% h.s.- $3d^7$, 28% h.s.- $3d^6$ with an electron delocalized over the catechol ligand, and the remainder ($\sim 3\%$) in l.s.- $3d^7$. The single-determinant description works quite well in the low-T phase with 98.5% of the weight residing in the l.s.- $3d^6$ state, and ($\sim 1.5\%$) residing in the intermediate spin $3d^6$ state. The small mixing between low-spin and higher-spin within a single configuration is due to the spin-orbit coupling. Therefore our low-T phase is exactly consistent with previous results of both ab initio calculations and experiment.

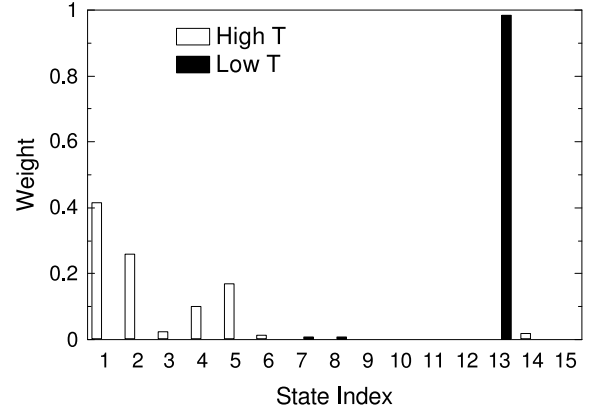


FIG. 3. Quantum weights of single determinants in Co(phen) ground state wavefunction. The vertical axis measures $|\alpha_i|^2$ where α_i are the variational coefficients. The model parameters correspond to $\Delta_{CT}^{ht} = -0.05$ eV and $\Delta_{CT}^{lt} = 0.42$ eV.

The most surprising aspect of these results is the resonance state in the high-T phase featuring large admixture with the h.s.- $3d^6$ state. There is a concomitant lowering of the energy such that the high-T phase is stabilized with respect to the low-T phase by ~ 0.4 eV. This entanglement of states would not be resolved by a mean-field theory like Hartree-Fock or DFT which both utilize a single-determinant groundstate composed of effective single-particle molecular orbitals.

An estimate should be made of the contribution of these correlations to the high-T ground state energy. We can separate out the contribution to the resonant energy lowering due to covalency by finding the energy difference between single determinant h.s.- $3d^7$ and the high-T ground state of our calculation. This will be the energy omitted by DFT calculations. For completeness, we include the possibility of the local electron tunneling to all excited states of the o-quinone ligands. This leads to an extra energy of ~ 0.2 eV that needs to be subtracted from the enthalpy difference between high- and low-T. This further reduces the 0.6 eV obtained from our relaxed DFT calculations. The small magnitude of the gap Δ_{CT} seems to be indicative of the system's proximity to a charge-transfer instability within our model. This also justifies the high degree of inter-configurational admixture in the high-T phase. Δ_{CT}^{ht} is nearly zero, slightly stabilized on the $n_d = 7$ side. Δ_{CT}^{lt} is larger and has changed signs, so $n_d = 6$ is stable. It will be seen in the next section that near-edge X-ray absorption data mandates some constraints as to where the high-T and low-T phases must reside relative to the instability.

D. XANES calculation

We find that data taken in X-ray absorption studies near the cobalt K-edge [10] corroborates the existence of the h.s.- $3d^6/3d^7$ mixed valence in the high-T state. We first discuss features of the experimental spectra. The on-set of the $1s$ - $4p$ absorption edge is ~ 7712.2 eV. The region of immediate interest to us is the low-intensity pre-edge interpreted as being composed of quadrupolar-allowed $1s$ - $3d$ transitions. (Actually, the Co ions lack inversion symmetry, though if restricted to just nearest neighbors there is an approximate mirror symmetry forbidding mixing between $4p$ and $3d$ states on site. The symmetry breaking by the SQ rings will yield an admixture of $4p$ and $3d$ which is likely to dominate the direct quadrupole matrix elements.) Data taken here provides a means to probe the nominal valence of the cobalt d -orbitals. As the temperature is reduced from T_{amb} , three main structures become apparent. The lowest energy feature is a shoulder at 7708 eV that loses spectral weight as the temperature is reduced. In the high-T phase, there is an intense peak at 7709.6 eV (which shifts up in energy by ~ 0.3 eV at lower temperatures) that gains $\sim 56\%$ in height. The third structure is a broad shoulder at ~ 7712.3 eV that all but completely disappears at low temperatures. While the first two structures have been assigned the $1s$ - $3d$ t_{2g} and $1s$ - $3d$ e_g transitions, this latter feature has yet to be identified.

We have used our model as the basis to calculate a theoretical XANES. It has been shown that the core electrons in transition metal and rare earth compounds do not efficiently screen the $1s$ -core hole left behind after the photoemission process. Thus the energies of the $3d$ -valence orbitals are significantly renormalized by Coulomb interaction with the core-hole. Treated perturbatively this amounts to a down-shift in energy for these orbitals. It has also been shown that in order to obtain good agreement with experimental data, a term must be added to the Hamiltonian that accounts for this core hole-valence electron interaction [30],

$$\delta H = -U_{dc} \sum_{\sigma} (1 - s_{\sigma}^{\dagger} s_{\sigma}) \sum_{\gamma} d_{\gamma\sigma}^{\dagger} d_{\gamma\sigma} \quad (6)$$

so our Hamiltonian in Eqns.(1) and (4) becomes H'

$$H' = H + \delta H \quad (7)$$

where s_{σ}^{\dagger} is the $1s$ -core electron creation operator, U_{dc} is the $1s$ - $3d$ Coulomb integral. The expression we use to calculate the X-ray absorption coefficient I for the $1s$ - $3d$ transition is the following which is similar to a weighted many-body density of states

$$I(\omega) = \sum_{\alpha'} |\langle \alpha' | \hat{T} | \Psi_0 \rangle|^2 \delta(\omega - E_{\alpha'} + E_0) \quad (8)$$

where ω is the incident photon energy, $E_{\alpha'}$ and $|\alpha'\rangle$ are the eigenstates of the Hamiltonian H' which is the same system described by H in the presence of the core-hole perturbation. E_0 and $|\Psi_0\rangle$ are the unperturbed ground state energy and wavefunction of our model calculation. \hat{T} is the transition operator

$$\hat{T} = W \sum_{\gamma\sigma} d_{\gamma\sigma}^{\dagger} s_{\sigma} \quad (9)$$

where we have neglected the orbital angular momentum dependence in W , the single-electron $1s$ - $3d$ transition matrix element.

We now discuss our results. Fig. 4(a) shows the spectra directly resulting from the model we have developed in the previous sections. The experimental XANES data has been superimposed over our results. Fig 4(b) depicts the result of a single-determinant l.s.- $3d^7$ low-T ground state for the purposes of comparison; since the tautomers are on the edge of the charge transfer instability, it might be possible by suitable selection of the redox passive ligand to access this low-spin Co(II) state. We have not estimated the broadening generated by electronic coupling to vibrational degrees of freedom and other contributing factors to finite lifetime effects. This limits our comparison to peak positions and relative weights.

We first discuss the high-T result. Fig 4(a) features four main temperature dependent peaks that may be directly related to the XAS data. We first note that our calculations reproduce the relative peak heights quite well. The peak at 7708.03 eV matches the shoulder found in that region and is the result of a down-spin $1s$ electron transferring into the t_{2g} . The shoulder feature has been previously assigned this transition. The peak at 7709.6 eV is the consequence of the transfer of a down-spin electron into an e_g level, also consistent with previous assignment. The energy distance between these two structures (~ 1.60 eV) is approximately the value of the ligand-field splitting which we would expect on the basis of the assigned transitions. There are two very closely-spaced peaks at 7710.79 and 7710.8 eV. These are transitions of down-spin electrons into the t_{2g} shell of $3d^7$ final states. Going up in energy by an amount equal to the ligand-field, we find a cluster of low-intensity peaks in the interval 7712.32 eV - 7712.42 eV that correspond to transfers into the e_g levels of the $3d^7$ final states. These latter features can be identified with the spectral weight centered about 7712.3 eV. This assignment is consistent with the disappearance of these peaks at low-T. To our knowledge, this is the first attempt to interpret these higher-energy satellite structures. This feature is thus unique to the type of highly admixed $3d^7/3d^6$ ground-state we are proposing for high-T. It can now be seen that the distance between the peaks at ~ 7709.6 eV and the cluster centered about 7712.4 eV (and also the distance between the peak at 7708.03 and the peaks at ~ 7710.8 eV) of ~ 2.5 eV provides a constraint for the value of U_{dc} - U_d .

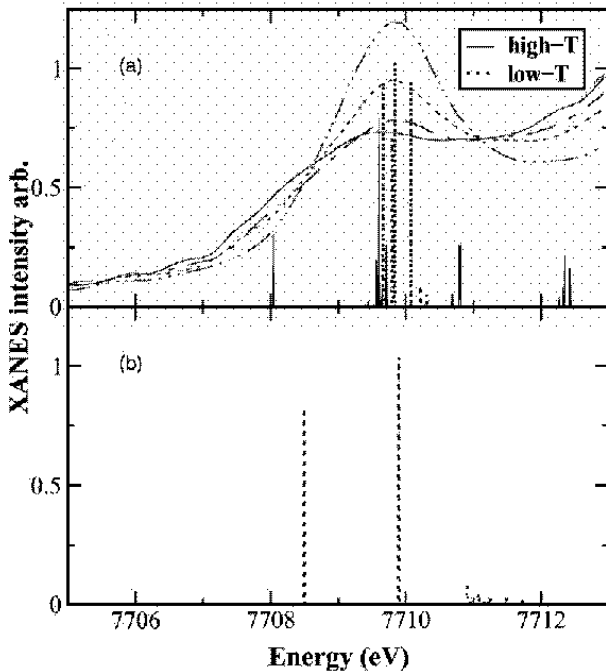


FIG. 4. (a) Model XANES calculation shown with experimental results for $\Delta_{CT}^{ht} = -0.05$ eV, $\Delta_{CT}^{lt} = 0.416$ eV, $E_{shift} = -1.05$ eV, and $U_{dc}-U_d = 2.36$ eV. Experimental curves show change in XANES with temperature. The solid line corresponds to the high-T phase and the (— · · · —) line is the low-T phase. (b) Low-T XANES calculation resulting from 1s.-3d⁷ groundstate. $\Delta_{CT}^{lt} = -0.004$ eV, $E_{shift} = 0.737$ eV, and $U_{dc}-U_d = 2.43$ eV

We have introduced an energy shift between the high- and low-T spectra, E_{shift} . The pragmatic intent is to fit the data. The underlying physical reasoning is twofold. We have used identical model parameters for both the high-T and low-T calculations, allowing only the distance dependence of the hopping integrals to change. We would expect some renormalization of some of these parameters due to effects like screening. More significantly, we have omitted some terms from our simple model Hamiltonian that would be quite different in the two geometries, e.g. cohesion energies, off-site Coulomb interactions, etc. Presumably, these would all have to be incorporated in such a shift. The low-T spectra in Fig 4(a) consists of 4 main peak structures concentrated in the region 7709.66 - 7710.8 eV. These are all associated with transferring a 1s-electron into the empty e_g shell of the 1s.-3d⁶ state. The heights and location of these agree quite well with the single broadened peak of experiment. The weights have not been altered relative to the high-T phase, giving very good consistency with experiment.

Fig 4(b) depicts a low-T XANES resulting from a 1s.-3d⁷ groundstate. This regime should be investigated since this manifold of states lies in close energetic proximity to the 1s.-3d⁶ singlet state. As shown, this low-T state can be accessed with only very slight tuning of the parameters. Such an interconversion would necessarily lack

metal-ligand CT and may be relevant for some species of tautomer which only exhibits spin-crossover on the metal site. While the central peak at 7709.9 eV agrees well with the data, there is the feature of augmented weight at low energies (~ 7708.05 eV) at low-T rather than the suppression seen in experiment. Since the absorption data seem to lack the twin peak structure (resulting from Hund's rule exchange splitting of up- and down- spin electron transitions to the singly-occupied e_g shell), this seems to be an untenable possibility for the low-T groundstate, at least with current choices for redox passive ligands.

IV. DOMAIN MODEL

As noted in the introduction, another problem with the traditional interpretation of valence tautomerism is the extraordinarily large entropy change (10-15 R) associated with the transition. However, it should be noted that this entropy change is inferred only indirectly from measurements of the magnetic susceptibility and optical absorption. On the other hand, measurements of the specific heat as a function of temperature done by Abakumov *et al* [12], which constitute a more direct measurement of the entropy, give a much lower entropy value (~ 1 R). This discrepancy leads us to examine the set of assumptions used to infer the entropy change from the susceptibility data. These can be summarized as follows.

At any given temperature T , the system is taken to be a two component mixture of the high-spin and low-spin forms of the molecule. The fraction of atoms in the high-spin form (f) is determined thermodynamically by minimizing the molar Gibbs free energy (G) which is given by

$$G = fG_{hs} + (1 - f)G_{ls} - RT[f\ln(f) + (1 - f)\ln(1 - f)] \quad (10)$$

where the last term is the entropy of mixing for a random two-component mixture. Minimizing the above equation with respect to f then gives us the functional form for the variation of f with T which used to infer the enthalpy (ΔH) and entropy (ΔS) change from the experimental data.

However the above derivation makes the assumption that the system can be described as a *random* two-component mixture. If there is clustering present in the system, then the above equations have to be modified. The simplest generalization which accounts for this is the domain model [13,14]. In this model, clustering is accounted for by considering domains with n number of molecules per domain (n is like a mean-field parameter corresponding to the average size of the domain, with $n = 1$ corresponding to the random two-component mixture). In this case the entropy of mixing is now given by

$$S_{mix} = -R/n [f \ln(f) + (1-f) \ln(1-f)] \quad (11)$$

Correspondingly the variation of f with temperature is

$$f = 1/[1 + e^{\frac{n\Delta H}{R}(1/T - 1/T_c)}] \quad (12)$$

The key point is that the values inferred from experiment have used the above form with $n = 1$ giving unphysically large values for ΔH and ΔS . However if there is clustering ($n > 1$) then the inferred value of ΔH (and correspondingly ΔS) will be lowered by a factor of n leading to more reasonable values. This leads us to the question: How can we infer what the appropriate value of n is? According to the domain model the answer can be obtained from specific heat measurements which should indicate a peak in the specific heat (C_p) centered around the transition temperature T_c . The ‘jump’ in the specific heat is given by $C_p(T_c) - \frac{1}{2}(C_{ls}(T_c) + C_{hs}(T_c))$ where $C_{ls}(T_c)(C_{hs}(T_c))$ is obtained by linear extrapolation at $T = T_c$ of the low(high) temperature specific heat values. The number of molecules per domain n is then related to this jump by

$$n = \frac{4 R T_c^2}{(\Delta H)^2} [C_p(T_c) - \frac{1}{2}(C_{ls}(T_c) + C_{hs}(T_c))] \quad (13)$$

It should be noted that the specific heat measurements will provide a direct measurement of ΔS (and thereby ΔH) and within the domain model this can be used to estimate n . For the tautomers, only one set of experiments done so far have measured the specific heat. From the data given by Abakumov *et al* for the bpy complex, we make the following estimates : The ‘jump’ in C_p corresponds to ~ 150 J/mol K which gives a change in entropy of $\Delta S \sim 1.2 R$. Using these values and the equation for n in the domain model we estimate $n \approx 50$. Thus the data for the specific heat shows evidence for clustering in the tautomers and is inconsistent with the original assumption of a random two-component mixture. The latter assumption leads to unphysically high inferred values of ΔH and ΔS and we propose that measurements of the specific heat can be used to resolve this discrepancy and to self-consistently check for the applicability of the domain model to the system.

V. CONCLUSIONS

In conclusion, we have extended the theory of cobalt valence tautomers to resolve some of the puzzles surrounding various data. In particular, we have shown that using fully relaxed density functional theory solutions goes halfway towards solving the mystery of large enthalpy values inferred from fits to optical absorption and magnetic susceptibility data. However, the relaxed DFT result of 0.6 eV is still off by a factor of 20 from the sole direct measurement of the enthalpy found in the

tautomer literature [12]. We have also shown that DFT provides little evidence for *net* charge transfer off the Co ion to the SQ ligands (indeed, the 3d weight increases modestly in the low-T phase!). On the other hand, a careful examination of the PDOS shows that the qualitative picture emerging from the formal valence arguments is still correct: the orbitals with the largest admixture of 3d - e_g symmetry are depopulated in going through the transition.

Next, we showed that a variational configuration interaction approach could produce a further lowering of the high-T enthalpy relative to the low-T entropy by producing a 30% admixture of Co(II) and Co(III) configuration. At the lowest variational order, we estimate an 0.2-0.3 eV lowering of energy due to electron correlation effects beyond DFT, which brings us within an order of magnitude of the directly observed enthalpy. This high-T state is intrinsically “CI”: no unitary transformation in the single particle orbital space can remove the multiconfiguration character. It is, in fact, a mixed valent state associated with the Co ion and the more extended and weakly correlated states of the SQ rings. We have also shown that this high-T state, when proper accounting is made for the core-hole interaction of the 3d electrons, can explain the previously observed spectral weight shift well above the dominant 1s-3d peak for high temperatures. The weight is ascribed to transitions to the admixed high spin Co(III) configuration.

Finally, we have proposed a domain model to account for the large $\Delta S, \Delta H$ values inferred from susceptibility and optical absorption data (as compared to direct measurement). In this view, the transition corresponds to a broadened first order phase transition of molecular clusters of order 20-60. In the dilute solvent, it might be possible to observe such clustering with elastic light scattering experiments. Although the heat capacity measurements in the interesting temperature range are difficult, we certainly would encourage further experiments on tautomers.

We hope to apply this combined DFT and VCI approach to other tautomer systems and to analyses of the closely related phenomena observed in the prosthetic complexes of metalloproteins and metalloenzymes.

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